(54) Simultaneous catalytic hydrocracking and hydrodewaxing of hydrocarbon oils with zeolite beta.

(57) Heavy oils are simultaneously subjected to hydrocracking and dewaxing using a catalyst based on zeolite beta together with a hydrogenation component; the process is able to effect a bulk conversion of the oil while, at the same time, yielding a low pour point product.

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SIMULTANEOUS CATALYTIC HYDROCRACKING AND
HYDRODEWAXING OF HYDROCARBON OILS WITH ZEOLITE BETA

This invention relates to a process for catalytically hydrocracking and hydrodewaxing hydrocarbon charge stocks to produce low pour point distillates and heavy fuel oils of reduced viscosity.

Catalytic dewaxing of hydrocarbon oils to reduce the temperature at which separation of waxy hydrocarbons occurs is a known process. A process of that nature is described in The Oil and Gas Journal dated January 6, 1975, at pages 69-73. Also, U.S. Patent 3,668,113 and U.S. Patent 3,894,938 describe dewaxing followed by hydrofinishing.

Reissue Patent No. 28,398 describes a process for catalytic dewaxing with a catalyst comprising a zeolite of the ZSM-5 type. A hydrogenation/dehydrogenation component may be present.

A process for hydrodewaxing a gas oil with a ZSM-5 type catalyst is described in U.S. Patent 3,956,102.

A mordenite catalyst containing a Group VI or a Group VIII metal is used to dewax a low V.I. distillate from a waxy crude, as described in U.S. Patent 4,110,056.

U.S. Patent 3,755,138 describes a process for mild solvent dewaxing to remove high quality wax from a lube stock, which is then catalytically dewaxed to specification pour point.

U.S. Patent 3,923,641 describes a process for hydrocracking napthas using zeolite beta as a catalyst.

Hydrocracking is a well known process and various zeolite catalysts have been employed in hydrocracking processes but although they may be effective in providing distillate yields having one or more properties consistent with the intended use of the distillate, these catalysts have, in general, suffered the disadvantage of not

providing product yields having good low temperature fluidity
characteristics, especially reduced pour point and viscosity. The
catalysts used for hydrocracking comprise an acid component and a
hydrogenation component. The hydrogenation component may be a noble
metal such as platinum or palladium or a non-noble metal such as
nickel, molybdenum or tungsten or a combination of these metals.
The acidic cracking component may be an amorphous material such as
an acidic clay or amorphous silica-alumina or, alternatively, a
zeolite. Large pore zeolites such as zeolites X and Y have been
conventionally used for this purpose because the principal
components of the feedstocks (gas oils, coker bottoms, reduced
crudes, recycle oils, FCC bottoms) are higher molecular weight
hydrocarbons which will not enter the internal pore structure of the
smaller pore zeolites and therefore will not undergo conversion.
So, if waxy feedstocks such as Amal Gas Oil are hydrocracked with a
large pore catalyst such as zeolite Y in combination with a
hydrogenation component, the viscosity of the oil is reduced by
cracking most of the 343°C+ material into material that boils at
343°C to 165°C. The remainder of the 343°C+ material that is not
converted contains the majority of the paraffinic components in the
feedstock because the aromatics are converted preferentially to the
paraffins. The unconverted 343°C+ material therefore retains a high
pour point so that the final product will also have a relatively
high pour point of about 10°C. Thus, although the viscosity is
reduced, the pour point is still unacceptable. Even if the
conditions are adjusted to give complete or nearly complete
conversion, the higher molecular weight hydrocarbons, which are
present in the feedstock, principally polycyclic aromatics, will be
subjected to cracking so as to lead to further reductions in the
viscosity of the product. The cracking products, however, will
include a substantial proportion of straight chain components
(n-paraffins) which, if they are of sufficiently high molecular

weight themselves, as they often are, will constitute a waxy component in the product. The final product may therefore be proportionately more waxy than the feedstock and, consequently, may have a pour point which is equally unsatisfactory or even more so. A further disadvantage of operating under high conversion conditions is that the consumption of hydrogen is increased. Attempts to reduce the molecular weight of these straight chain paraffinic products will only serve to produce very light fractions for example, propane, so decreasing the desired liquid yield.

In the dewaxing process, on the other hand, a small pore zeolite or a shape selective zeolite such as ZSM-5 is used as the acidic component of the catalyst and the normal and slightly branched chain paraffins which are present in the feedstock will be able to enter the internal pore structure of the zeolite so that they will undergo conversion. The major proportion -- typically about 70 percent of the feedstock -- boiling above 343°C will remain unconverted because the bulky aromatic components, especially the polycyclic aromatics, are unable to enter the zeolite. The paraffinic waxy components will therefore be removed so as to lower the pour point of the product but the other components will remain so that the final product will have an unacceptably high viscosity even though the pour point may be satisfactory.

It has now been found that heavy hydrocarbon oils may be simultaneously hydrocracked and hydrodewaxed to produce a liquid product of satisfactory pour point and viscosity. This desirable result is obtained by the use of a catalyst which contains zeolite beta as an acidic component to induce the cracking reactions. The catalyst preferably includes a hydrogenation component to induce hydrogenation reactions. The hydrogenation component may be a noble metal or a non-noble metal and is suitably of a conventional type, for example nickel, tungsten, cobalt, molybdenum or combinations of these metals.

In accordance with the invention, there is provided a
process for cracking and dewaxing a heavy hydrocarbon oil which
comprises contacting the oil with a catalyst comprising zeolite beta.

In the process of the invention, the hydrocarbon feedstock
is heated with the catalyst under conversion conditions which are
appropriate for hydrocracking. During the conversion, the aromatics
and naphthenes which are present in the feedstock undergo
hydrocracking reactions such as dealkylation, ring opening and
cracking, followed by hydrogenation. The long chain paraffins which
are present in the feedstock, together with the paraffins produced
by the hydrocracking of the aromatics are, in addition, converted
into products which are less waxy than the straight chain
n-paraffins, thereby effecting a simultaneous dewaxing. The use of
zeolite beta is believed to be unique in this respect, producing not
only a reduction in the viscosity of the product by hydrocracking
but also a simultaneous reduction in pour point by catalytic
hydrodewaxing.

The process enables heavy feedstocks such as gas oils
boiling above 343°C to be converted to distillate range products
boiling below 343°C but in contrast to prior processes using large
pore catalysts such as zeolite Y, the consumption of hydrogen will
be reduced even though the product will conform to the desired
specifications for pour point and viscosity. In contrast to
dewaxing processes using shape selective catalysts such as zeolite
ZSM-5, the bulk conversion including cracking of aromatic components
takes place, ensuring acceptably low viscosity in the distillate
range product. Thus, the present process is capable of effecting a
bulk conversion together with a simultaneous dewaxing. Moreover,
this is achieved with a reduced hydrogen consumption as compared to
the other types of process. It is also possible to operate at
partial conversion, thus effecting economies in hydrogen consumption
while still meeting pour point and viscosity requirements. The

process also achieves enhanced selectivity for the production of distillate range materials; the yield of gas and products boiling below the distillate range is reduced.

As mentioned above, the process combines elements of hydrocracking and dewaxing. The catalyst used in the process has an acidic component and a hydrogenation component which may be conventional in type. The acidic component comprises zeolite beta, which is described in U.S. Patents 3,303,069 and Re 28,341 and reference is made to those patents for details of this zeolite and its preparation.

Zeolite beta is a crystalline aluminosilicate zeolite having a pore size greater than 5 Angstroms. The composition of the zeolite as described in U.S. Patents 3,303,069 and Re 28,341, in its as synthesized form may be expressed as follows:

$$[XNa(1.0\pm0.1-X)TEA]AlO_2 \cdot YSiO_2 \cdot WH_2O$$

where X is less than 1, preferably less than 0.7; TEA represents the tetraethylammonium ion; Y is greater than 5 but less than 100 and W is up to about 60 (it has been found that the degree of hydration may be higher than originally determined, where W was defined as being up to 4), depending on the degree of hydration and the metal cation present. The TEA component is calculated by differences from the analyzed value of sodium and the theoretical cation-to-structural aluminum ratio of unity.

In the fully base-exchanged form, beta has the composition:

$$[\frac{X}{n}M(1\pm0.1-X)H] \cdot AlO_2 \cdot YSiO_2 \cdot WH_2O$$
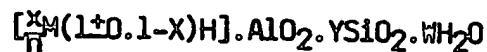
where X, Y and W have the values listed above and n is the valence of the metal M.

In the partly base-exchanged form which is obtained from
the initial sodium form of the zeolite by ion exchange without
calcining, zeolite beta has the formula:

$$[\tfrac{X}{n}M(1\pm0.1\text{-}X)TEA]AlO_2 \cdot YSiO_2 \cdot WH_2O$$

When it is used in the catalysts, the zeolite is at least
partly in the hydrogen form in order to provide the desired acidic
functionality for the cracking reactions which are to take place.
It is normally preferred to use the zeolite in a form which has
sufficient acidic functionality to give it an alpha value of 1 or
more. The alpha value, a measure of zeolite acidic functionality,
is described, together with details of its measurement in U.S.
Patent 4,016,218 and in J. Catalysis, Vol. VI, pages 278-287 (1966)
and reference is made to those publications for such details. The
acidic functionality may be controlled by base exchange of the
zeolite, especially with alkali metal cations such as sodium, by
steaming or by control of the silica:alumina ratio of the zeolite.

When synthesized in the alkali metal form, zeolite beta may
be converted to the hydrogen form by formation of the intermediate
ammonium form as a result of ammonium ion exchange and calcination
of the ammonium form to yield the hydrogen form. In addition to the
hydrogen form, other forms of the zeolite wherein the original
alkali metal has been reduced to less than about 1.5 percent by
weight may be used. Thus, the original alkali metal of the zeolite
may be replaced by ion exchange with other suitable metal cations
including, by way of example, nickel, copper, zinc, palladium,
calcium and rare earth metals.

Zeolite beta, in addition to possessing a composition as
defined above, may also be characterized by its X-ray diffraction
data which are set out in U.S. Patents 3,308,069 and Re. 28,341.
The significant d values (Angstroms, radiation: K alpha doublet of
copper, Geiger counter spectrometer) are as shown in Table 1 below:

TABLE 1

d Values of Reflections in Zeolite Beta

11.40 + 0.2

7.40 + 0.2

6.70 + 0.2

4.25 + 0.1

3.97 + 0.1

3.00 + 0.1

2.20 + 0.1

The preferred forms of zeolite beta for use in the process are the high silica forms, having a silica:alumina ratio of at least 30:1. It has been found, in fact, that zeolite beta may be prepared with silica:alumina ratios above the 100:1 maximum specified in U.S. Patents 3,308,069 and Re. 28,341 and these forms of the zeolite provide the best performance in the process. Ratios of at least 50:1 and preferably at least 100:1 or even higher, for example e.g. 250:1, 500:1 may be used.

The silica:alumina ratios referred to herein are the structural or framework ratios, that is, the ratio of the SiO_4 to the AlO_4 tetrahedra which together constitute the structure of which the zeolite is composed. It should be understood that this ratio may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by the thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain tr atments such as the dealuminization method described below, which

result in the presence of ionic aluminum free of the zeolite structure, are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

The silica:alumina ratio of the zeolite may be determined by the nature of the starting materials used in its preparation and their quantities relative one to another. Some variation in the ratio may therefore be obtained by changing the relative concentration of the silica precursor relative to the alumina precursor but definite limits in the maximum obtainable silica:alumina ratio of the zeolite may be observed. For zeolite beta this limit is usually about 100:1 (although higher ratios may be obtained) and for ratios above this value, other methods are usually necessary for preparing the desired high silica zeolite. One such method comprises dealumination by extraction with acid and that method comprises contacting the zeolite with an acid, preferably a mineral acid such as hydrochloric acid. The dealuminization proceeds readily at ambient and mildly elevated temperatures and occurs with minimal losses in crystallinity, to form high silica forms of zeolite beta with silica:alumina ratios of at least 100:1, with ratios of 200:1 or even higher being readily attainable.

The zeolite is conveniently used in the hydrogen form for the dealuminization process although other cationic forms may also be employed, for example, the sodium form. If these other forms are used, sufficient acid should be employed to allow for the replacement by protons of the original cations in the zeolite. The amount of zeolite in the zeoloite/acid mixture should generally be from 5 to 60 percent by weight.

The acid may be a mineral acid, i.e., an inorganic acid or an organic acid. Typical inorganic acids which can be employed include mineral acids such as hydrochloric, sulfuric, nitric and

phosphoric acids, peroxydisulfonic acid, dithionic acid, sulfamic acid, peroxymonosulfuric acid, amidodisulfonic acid, nitrosulfonic acid, chlorosulfuric acid, pyrosulfuric acid, and nitrous acid. Representative organic acids which may be used include formic acid, trichloroacetic acid, and trifluoroacetic acid.

The concentration of added acid should be such as not to lower the pH of the reaction mixture to an undesirably low level which could affect the crystallinity of the zeolite undergoing treatment. The acidity which the zeolite can tolerate will depend, at least in part, upon the silica/alumina ratio of the starting material. Generally, it has been found that zeolite beta can withstand concentrated acid without undue loss in crystallinity but as a general guide, the acid will be from 0.1 N to 4.0 N, usually 1 to 2 N. These values hold good regardless of the silica:alumina ratio of the zeolite beta starting material. Stronger acids tend to effect a relatively greater degree of aluminum removal than weaker acids.

The dealuminization reaction proceeds readily at ambient temperatures but mildly elevated temperatures may be employed e.g. up to 100°C. The duration of the extraction will affect the silica:alumina ratio of the product since extraction, being diffusion controlled, is time dependent. However, because the zeolite becomes progressively more resistant to loss of crystallinity as the silica:alumina ratio increases i.e. it becomes more stable as the aluminum is removed, higher temperatures and more concentrated acids may be used towards the end of the treatment than at the beginning without the attendant risk of losing crystallinity.

After the extraction treatment, the product is water-washed free of impurities, preferably with distilled water, until the effluent wash water has a pH within the approximate range of 5 to 8.

The crystalline dealuminized products obtained by the method of this invention have substantially the same crystallographic structure as that of the starting aluminosilicate zeolite but with increased silica:alumina ratios. The formula of the dealuminized zeolite beta will therefore be

$$[\tfrac{X}{n}M(1\pm0.1-X)H]AlO_2 \cdot YSiO_2 \cdot WH_2O$$

where X is less than 1, preferably less than 0.75, Y is at least 100, preferably at least 150 and W is up to 60. M is a metal, preferably a transition metal or a metal of Groups IA, 2A or 3A, or a mixture of metals. The silica:alumina ratio, Y, will generally be in the range of 100:1 to 500:1, more usually 150:1 to 300:1, for example 200:1 or more. The X-ray diffraction pattern of the dealuminized zeolite will be substantially the same as that of the original zeolite, as set out in Table 1 above.

If desired, the zeolite may be steamed prior to acid extraction so as to increase the silica:alumina ratio and render the zeolite more stable to the acid. The steaming may also serve to increase the ease with which the acid is removed and to promote the retention of crystallinity during the extraction procedure.

The zeolite beta is preferably used in combination with a hydrogenating component which is usually derived from a metal of Groups VA, VIA or VIIIA of the Periodic Table. Preferred non-noble metals are such as tungsten, vanadium, molybdenum, nickel, cobalt, chromium, and manganese, and the preferred noble metals are platinum, palladium, iridium and rhodium. Combinations of non-noble metals such as cobalt-molybdenum, cobalt nickel, nickel-tungsten or cobalt-nickel-tungsten are exceptionally useful with many feedstocks and, in a preferred combination, the hydrogenation component comprises from 0.7 to about 7 wt.% nickel and 2.1 to about 21 wt.% tungsten, expressed as metal. The hydrogenation component can be exchanged onto the zeolite, impregnated into it or physically

admixed with it. If the metal is to be impregnated into or
exchanged onto the zeolite, it may be done, for example, by treating
the zeolite with a platinum metal-containing ion. Suitable platinum
compounds include chloroplatinic acid, platinous chloride and
various compounds containing the platinum ammine complex.

The catalyst may be treated by conventional pre-sulfiding
treatments, for example by heating in the presence of hydrogen
sulfide, to convert oxide forms of the metals such as CoO or NiO to
their corresponding sulfides.

The metal compounds may be either compounds in which the
metal is present in the cation of the compound and compounds in
which it is present in the anion of the compound. Both types of
compounds can be used. Platinum compounds in which the metal is in
the form of a cation or cationic complex, for example,
$Pt(NH_3)_4Cl_2$, are particularly useful, as are anionic complexes
such as the vanadate and metatungstate ions. Cationic forms of
other metals are also very useful since they may be exchanged onto
the zeolite or impregnated into it.

Prior to use the zeolite should be dehydrated at least
partially. This can be done by heating to a temperature in the
range of 200°C to 600°C in air or an inert atmosphere such as
nitrogen for 1 to 48 hours. Dehydration can also be performed at
lower temperatures merely by using a vacuum, but a longer time is
required to obtain a sufficient amount of dehydration.

It may be desirable to incorporate the catalyst in another
material resistant to the temperature and other conditions employed
in the process. Such matrix materials include synthetic and
naturally occurring substances such as inorganic materials, for
example clay, silica and metal oxides. The latter may be either
naturally occurring or in the form of gelatinous precipitates or
gels including mixtures of silica and metal oxides. Naturally
occurring clays can be composited with the zeolite including those

of the montmorillonite and kaolin families. The clays can be used
in the raw state as originally mined or initially subjected to
calcination, acid treatment or chemical modification.

The zeolite may be composited with a porous matrix
material, such as alumina, silica-alumina, silica-magnesia,
silica-zirconia, silica-thoria, silica-berylia, silica-titania, as
well as terniary compositions, such as silica-alumina-thoria,
silica-alumina-zirconia, magnesia and silica-magnesia-zirconia. The
matrix may be in the form of a cogel. The relative proportions of
zeolite component and inorganic oxide gel matrix on an anhydrous
basis may vary widely with the zeolite content ranging from 10 to
99, more usually 25 to 80, percent by weight of the dry composite.
The matrix itself may possess catalytic properties, generally of an
acidic nature.

The feedstock for the process of the invention comprises a
heavy hydrocarbon oil such as a gas oil, coker tower bottoms
fraction, reduced crude, vacuum tower bottoms, deasphalted vacuum
resids, FCC tower bottoms, or cycle oils. Oils derived from coal,
shale, or tar sands may also be treated in this way. Oils of this
kind generally boil above 343°C although the process is also useful
with oils which have initial boiling points as low as 260°C. These
heavy oils comprise high molecular weight long chain paraffins and
high molecular weight aromatics with a large proportion of fused
ring aromatics. During the processing, the fused ring aromatics and
naphthenes are cracked by the acidic catalyst and the paraffinic
cracking products, together with paraffinic components of the
initial feedstock undergo conversion to iso-paraffins with some
cracking to lower molecular weight materials. Hydrogenation of
unsaturated side chains on the monocyclic cracking residues of the
original polycyclics is catalyzed by the hydrogenation component to
form substituted monocyclic aromatics which are highly desirable end
products. The heavy hydrocarbon oil feedstock will normally contain

a substantial amount boiling above 230°C and will normally hav an initial boiling point of about 290°C, more usually about 340°C. Typical boiling ranges will be about 340° to 565°C or about 340°C to 510°C but oils with a narrower boiling range may, of course, be processed, for example, those with a boiling range of about 340° to 455°C. Heavy gas oils are often of this kind as are cycle oils and other non-residual materials. It is possible to co-process materials boiling below 260°C but the degree of conversion will be lower for such components. Feedstocks containing lighter ends of this kind will normally have an initial boiling point above 150°C.

The process is of particular utility with highly paraffinic feeds because, with feeds of this kind, the greatest improvement in pour point may be obtained. However, most feeds will contain a certain content of polycyclic aromatics.

The process is carried out under conditions similar to those used for conventional hydrocracking although the use of the highly siliceous zeolite catalyst permits the total pressure requirements to be reduced. Process temperatures of 230°C to 500°C may conveniently be used although temperatures above 425°C will normally not be employed as the thermodynamics of the hydrocracking reactions become unfavorable at temperatures above this point. Generally, temperatures of 300°C to 425°C will be employed. Total pressure is usually in the range of 500 to 20,000 kPa and the higher pressures within this range over 7000 kPa will normally be preferred. The process is operated in the presence of hydrogen and hydrogen partial pressures will normally be from 600 to 6000 kPa. The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) will normally be from 10 to 3500 n.l.l^{-1}. The space velocity of the feedstock will normally be from 0.1 to 20 LHSV, preferably 0.1 to 10 LHSV. At low conversions, the n-paraffins in the feedstock will be converted in preference to the iso-paraffins but at higher conversions under more severe conditions

the iso-paraffins will also be converted. The product is low in fractions boiling below 150°C and in most cases the product will have a boiling range of 150° to 340°C.

The conversion may be carried out by contacting the feedstock with a fixed stationary bed of catalyst, a fixed fluidized bed or with a transport bed. A simple configuration is a trickle-bed operation in which the feed is allowed to trickle through a stationary fixed bed. With such a configuration, it is desirable to initiate the reaction with fresh catalyst at a moderate temperature which is of course raised as the catalyst ages, in order to maintain catalytic activity. The catalyst may be regenerated by contact at elevated temperature with hydrogen gas, for example, or by burning in air or other oxygen-containing gas.

A preliminary hydrotreating step to remove nitrogen and sulfur and to saturate aromatics to naphthenes without substantial boiling range conversion will usually improve catalyst performance and permit lower temperatures, higher space velocities, lower pressures or combinations of these conditions to be employed.

The process of the invention is illustrated by the following Examples. All parts and proportions in these Examples are by weight unless stated to the contrary.

EXAMPLE 1

This Example illustrates the preparation of a catalyst.

A mixture of zeolite beta ($SiO_2/Al_2O_3=30$) having a crystallite size of less than 0.05 microns and an equal amount gamma alumina on an anhydrous basis was extruded to form 1.5 mm. pellets. The pellets were calcined at 540°C in nitrogen, magnesium exchanged, and then calcined in air.

One hundred grams of the air-calcined extrudate was impregnated with 13.4 grams of ammonium metatungstate (72.3%W) in 60 ml of water, followed by drying at 115°C and calcination in air at 540°C. The extrudate was then impregnated with 15.1 grams of nickel

hexahydrate in 60 ml of water, and the wet pellets dried and
calcined at 540°C.

The final catalyst had a nickel content of about 4 weight
percent as NiO and a calculated tungsten content of about 10.0
weight percent as WO_3. The sodium content was less than 0.5
weight percent as sodium oxide.

Example 2

This example describes the preparation of high silica
zeolite beta.

A sample of zeolite beta in its as-synthesized form and
having a silica:alumina ratio of 30:1 was calcined in flowing
nitrogen at 500°C for 4 hours, followed by air at the same
temperature for 5 hours. The calcined zeolite was then refluxed
with 2N hydrochloric acid at 95°C for one hour to produce a
dealuminized, high silica form of zeolite beta having a
silica:alumina ratio of 280:1, an alpha value of 20 and a
crystallinity of 80 percent relative to the original, assumed to be
100 percent crystalline.

The zeolite was exchanged to the ammonium form with 1 N
ammonium chloride solution at 90°C reflux for an hour followed by
the exchange with 1 N magnesium chloride solution at 90°C reflux for
an hour. Platinum was introduced into the zeolite by ion-exchange
of the tetrammine complex at room temperature. The metal exchanged
zeolite was thoroughly washed and oven dried by air calcination at
350°C for 2 hours. The finished catalyst contained 0.6 percent
platinum and was pelletted, crushed and sized to 0.35 to 0.5 mm.

EXAMPLES 3-5

The catalyst of Example 1 was evaluated for the catalytic
conversion of an Arab Light gas oil (HVGO) having a boiling range of
354° to 580°C. For comparison, a magnesium exchanged zeolite Y
(SiO_2/Al_2O_3=5) catalyst was also composed by extrusion with an
equal amount of gamma alumina and impregnation to contain 4 weight
percent nickel and 10 weight percent tungsten.

The feedstock composition, conditions used and product analysis are given in Table 2 below.

TABLE 2

Hydrocracking/Dewaxing

Example No.	Feed	3	4
Catalyst	-	Mg Beta	MgY
Conditions:			
Temp.,°C	-	423	414
Pressure, kPa	-	7000	7000
LHSV, hr^{-1}	-	0.54	0.71
H$_2$, n.l.l.$^{-1}$	-	1674	1318
H$_2$ Consumption, n.l.1^{-1}	-	125	193
343°C + Conversion, wt. %	-	62.2	56.6
Properties:			
Dry Gas + C$_4$	-	3.5	4.1
C$_5$ - 165°C Naptha, wt. %	-	16.6	24.7
165°C - 343°C Distillate, wt. %	-	40.6	26.3
343°C + wt. %	100	37.8	44.0
343°C + Pour Point, °C	40	-1	35
343°C + 95% TBP, °C	552	468	528
343°C+ Properties:			
Gravity, °API	22.0	--	--
Hydrogen, Wt.%	12.07	12.7	13.7
Sulfur	2.45	0.04	0.03
Nitrogen	600	80	18
Pour Point °C	40	-1	35
Paraffins, vol.%	24.0	31	40
Naphthenes, vol. %	25.3	28	35
Aromatics, vol.%	50.7	41	25

As shown above in Table 2, at a relatively high conversion of approximately 60 percent, the beta catalyst significantly lowered the pour point of the 343°C+ product whereas the products obtained with zeolite Y catalysts remained waxy. Additionally, the beta catalyst converted considerably more of the high boiling components in the charge which resulted in a 343°C+ product endpoint about 55°C

lower than obtained with the catalyst of Example 4. The hydrogen consumption was also notably lower whether on an absolute basis or relative to conversion.

For comparison with Example 3, a similar Arab Light HVGO having a boiling range of 370° to 550°C was hydrocracked over a rare earth exchanged ultrastable zeolite Y ($SiO_2:Al_2O_3$ = 75). The zeolite was prepared by steam calcination and acid dealuminization of zeolite Y to a framework $SiO_2:Al_2O_3$ ratio of 75:1, followed by rare earth exchange, extrusion with an equal amount of gamma alumina and impregnation to contain 2 weight percent nickel and 7 weight percent tungsten.

The feedstock composition, conditions used and product analysis are given in Table 3 below.

TABLE 3

Hydrocracking over REY Catalyst

Example No.	Feed	5
Conditions:		
Temp., $^{\circ}C$	—	416
Pressure, kPa	—	7000
LHSV, hr^{-1}	—	0.67
H_2, n.l.l.$^{-1}$	—	1338
H_2 Consumption, n.l.l^{-1}	—	143
$343^{\circ}C$ + Conversion, wt. %	—	60.4
Properties:		
Dry Gas + C_4	—	3.6
C_5 – $165^{\circ}C$ Naptha, wt. %	—	14.2
$165^{\circ}C$ – $343^{\circ}C$ Distillate, wt. %	—	41.4
$343^{\circ}C$ + wt. %	100	39.6
$343^{\circ}C$ + Pour Point, $^{\circ}C$	43	32
$343^{\circ}C$ + 95% TBP, $^{\circ}C$	540	504
$343^{\circ}C$+ Properties:		
Gravity, $^{\circ}API$	21.7	—
Hydrogen, Wt.%	12.17	13.26
Sulfur	2.41	0.01
Nitrogen	550	33
Pour Point $^{\circ}C$	43	32
Yields:		
Paraffins, vol.%	19	41
Naphthenes, vol. %	27	26
Aromatics, vol.%	54	33

CLAIMS

1. A process for cracking and dewaxing a heavy hydrocarbon oil which comprises contacting the oil with a catalyst comprising zeolite beta.

2. A process according to claim 1, in which the oil is contacted in the presence of hydrogen with a catalyst comprising (i) zeolite beta as an acidic component and (ii) a hydrogenation component.

3. A process according to claim 2, in which the zeolite beta has a silica:alumina ratio greater than 50:1.

4. A process according to claim 2 or claim 3, in which the hydrogenation component comprises nickel, tungsten, cobalt, molybdenum or a mixture of any two or more such metals.

5. A process according to claim 4, in which the hydrogenation component comprises nickel and tungsten.

6. A process according to claim 2 or claim 3, in which the hydrogenation component comprises platinum, palladium, iridium, rhodium or a combination of any two or more such metals.

7. A process according to any one of claims 1 to 6, in which the oil has an initial boiling point above 290°C.

8. A process according to claim 7, in which the oil has an initial boiling point above 340°C.

9. A process according to claim 8, in which the oil has a boiling point from 340° to 565°C.

10. A process according to any one of claims 2 to 9, in which the oil is contacted with the catalyst in the presence of hydrogen gas at a temperature of 230°C to 500°C, a pressure of 500 to 20,000 kPa, a space velocity of 0.1 to 20 and a hydrogen circulation rate of 10 to 3500 $n.l.l^{-1}$.

0591H/0023H

	DOCUMENTS CONSIDERED TO BE RELEVANT		EP 83302774.1	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	**CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)**	
A	<u>DE - A1 - 2 625 340</u> (MOBIL OIL CORPORATION) * Claim 16; page 1, line 1 - page 17, line 8; example 11 * ----	1,3	C 10 G 49/08 C 10 G 47/18 B 01 J 29/28	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 10 G 45/00

C 10 G 49/00

C 10 G 47/00

B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	25-08-1983	STÖCKLMAYER